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Soil Biology & Biochemistry 38 (2006) 477–488

Soil Biology & Biochemistry

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Temperature, water content and wet–dry cycle effects on DOC production and carbon mineralization in agricultural peat soils

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Received 30 March 2004; received in revised form 26 May 2005; accepted 1 June 2005
Available online 11 July 2005

Abstract

Agricultural peat soils in the Sacramento-San Joaquin Delta, California have been identified as an important source of dissolved organic carbon (DOC) and trihalomethane precursors in waters exported for drinking. The objectives of this study were to examine the primary sources of DOC from soil profiles (surface vs. subsurface), factors (temperature, soil water content and wet–dry cycles) controlling DOC production, and the relationship between C mineralization and DOC concentration in cultivated peat soils. Surface and subsurface peat soils were incubated for 60 d under a range of temperature (10, 20, and 30 °C) and soil water contents (0.3–10.0 g-water g-soil^{-1}). Both CO_2–C and DOC were monitored during the incubation period. Results showed that significant amount of DOC was produced only in the surface soil under constantly flooded conditions or flooding/non-flooding cycles. The DOC production was independent of temperature and soil water content under non-flooded condition, although CO_2 evolution was highly correlated with these parameters. Aromatic carbon and hydrophobic acid contents in surface DOC were increased with wetter incubation treatments. In addition, positive linear correlations ($r^2 = 0.87$) between CO_2–C mineralization rate and DOC concentration were observed in the surface soil, but negative linear correlations ($r^2 = 0.70$) were observed in the subsurface soil. Results imply that mineralization of soil organic carbon by microbes prevailed in the subsurface soil. A conceptual model using a kinetic approach is proposed to describe the relationships between CO_2–C mineralization rate and DOC concentration in these soils.

Keywords: CO_2 evolution; Dissolved organic carbon; Sacramento-San Joaquin Delta; Soil organic carbon; SUVA; XAD fractionation

1. Introduction

Agricultural drainage from cultivated peat soils in the Sacramento-San Joaquin Delta has been identified as a significant source of dissolved organic carbon (DOC) in Delta waterways (Amy et al., 1990). The Delta is a source of exported drinking water for over 22 million people in California. High DOC in drinking water sources is of concern because DOC causes color and odor problems, and more importantly, is a precursor of carcinogenic and mutagenic disinfection byproducts such as trihalomethanes and haloacetic acids (Krasner, 1999). On a quarterly basis beginning with the winter season, agricultural drainage was estimated to contribute 71, 27, 26, and 23 Mg C d^{-1}, respectively, into Delta waterways (Jassby and Cloern, 2000). In addition, these agricultural peat lands, which originally were marshes and swamps prior to drainage, are subjected to microbial oxidation resulting in severe land subsidence (Rojstaczer and Deverel, 1995). Net subsidence rates for Delta peat soils range from 0.46 to 1.06 cm yr^{-1} (Deverel and Rojstaczer, 1996). Continued subsidence increases the potential for flooding due to levee breaks. Delta peat soils are an important agricultural resource, but also a major non-point source of DOC and disinfection byproduct precursors in Delta waterways.

Variations in DOC release and CO_2 evolution from Delta peat soils result from current agricultural practices and the Mediterranean climate (CDWR, 1994; Rojstaczer et al., 1991). Sub-irrigation with high evapoconcentration rates in summer and salt leaching practices in winter dramatically change soil salinity and water content, creating seasonal and short-term wet–dry cycles in soils (CDWR, 1994; Fujii

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doi:10.1016/j.soilbio.2005.06.005

et al., 1998). Fujii et al. (1998) showed that soil temperature in surface (0.15–0.5 m depth) and subsurface (1.5–2 m depth) zones varied from 12 to 33 °C and 13 to 27 °C, respectively. Electrical conductivity of 7 dS m^{-1} or greater was recorded in soil water from the surface soil (Fujii et al., 1998). The wet–dry cycle can strongly affect soil carbon transformations (Fierer and Schimel, 2002). Wet–dry cycles affect soil aeration and create alternating anaerobic and aerobic conditions that promote a diversity of microorganisms (Fierer et al., 2003b). Although the surface peat soils have been exposed to long periods of aerobic decay and may be resistant to further decay (Hogg et al., 1992), wet–dry cycles may enhance decomposition of refractory peat materials. Laboratory and field experiments both showed an increase in DOC concentrations after soils were exposed to wet–dry cycles (Fierer and Schimel, 2002; Lundquist et al., 1999). However, studies evaluating the effects of wet–dry cycles on both DOC and CO_2 production from agricultural peat soils are limited.

Previous studies indicated that soil temperature, water content, and wet–dry cycles affect decomposition rates of soil organic carbon (SOC) (Fierer and Schimel, 2002; Hogg et al., 1992; Howard and Howard, 1993; Kowalenko et al., 1978), and could also affect the quantity as well as the chemical characteristics of DOC (Blodau et al., 2004; Chow et al., 2003; Christ and David, 1996; Kalbitz et al., 2000; Lundquist et al., 1999). Positive correlations were observed between C mineralization rate and DOC concentration (Cook and Allan, 1992b; Lundquist et al., 1999). However, studies examining the linkage between C mineralization rate and DOC concentrations under variable temperature, water content and wet–dry cycles are few, particularly in agricultural peat soils. Furthermore, most peat soils in the Delta have a relatively shallow groundwater table (1–2 m depth). Soil above the water table is composed of oxidized, well-decomposed peat materials, whereas soil below the water table is generally reduced and consists of fibrous peat (Fujii et al., 1998). Studies showed that C mineralization of surface and subsurface soils responded differently upon changes of environmental parameters (Fierer et al., 2003a). Therefore, DOC and CO_2 production from both soil layers needs to be examined in order to understand the C dynamics of these peat soils.

The objectives of this study were to identify the source of DOC produced in soil profiles (surface vs. subsurface), determine factors (temperature, soil water content and wet–dry cycles) controlling DOC production and composition, and examine relationships between C mineralization and DOC concentration in cultivated peat soils from the Sacramento-San Joaquin Delta. Understanding the factors affecting carbon cycling, particularly DOC and CO_2 production, under various agricultural practices is essential for land management and water quality improvement.

2. Materials and experimental methods

2.1. Site description, soil sampling and preparation

Soil samples from an agricultural field on Twitchell Island in the west-central Delta were collected for this study. The site was chosen as it represents typical land-use practices in the Delta and it was the site of a previous study by Fujii et al. (1998). Corn was grown in summer and soils were flooded for 1–2 months to leach salts during the winter. Soils were classified as a Rindge muck (Typic Haplosaprist), with oxidized, well-decomposed peat from the surface to about 0.5 m depth, and reduced, fibrous peat dominating below about 1–1.5 m depth. Sampling was done in November, after the growing season but before flooding for salt leaching. Soil samples were collected from 0–0.5 to 2.5–3 m, to represent surface oxidized peat soil and subsurface reduced peat soil, respectively. Surface soil was collected after removal of crop residues from the surface. Subsurface soil was collected from a 3-m deep trench dug with a backhoe. Fibrous peat samples were taken from the walls of the trench and promptly placed into plastic bags, purged with N_2 gas, and sealed to preserve their reduced condition.

Before incubation, the surface soil was washed with a synthesized carbon-free solution containing 3.83 mM NaCl and 0.59 mM $CaCl_2$ to mimic salt leaching practices in the field. The synthesized solution had an electrical conductivity at 25 °C (EC_{25}) of 0.5 dS m^{-1} and a sodium adsorption ratio (SAR) of 5, representing typical soil salinity and sodicity in the field after flooding. A 5.5 kg sample of air-dried surface soil was placed in a 10 liter plastic bucket with a Whatman #1 filter paper and a 0.1 mm grid stainless steel screen at the bottom. The synthesized solution was pumped through the column at 100 ml min^{-1} using a peristaltic pump. Effluents were collected every 10 liter for ultra-violet absorbance at 254 nm (UVA) and EC_{25} analysis. Dissolved oxygen was continually measured in effluent from the soil column and it did not go below 5 mg l^{-1} during the washing procedure. This washing procedure was stopped when the differences of both UVA and EC_{25} were 5% or less from the previous sampling period. A total of 250 liter of effluent was collected and the DOC concentration was stable at about 25 mg l^{-1}. The treated soil was air-dried and sieved through a 2-mm sieve. Subsurface soil was not pre-washed and was sieved through a 9.5-mm sieve in a glove bag filled with N_2 in order to preserve its reduced conditions and to minimize tearing of the fibrous materials. Both soils were stored at 4 °C in the dark until further use.

2.2. Experimental design

Surface and subsurface soils were used for a batch incubation experiment to determine the effects of temperature, soil water content (θ_g), and wet–dry cycles on C mineralization and DOC production. The treatment

Table 1
Temperature and soil water content used in the incubation experiments

Soil Used	Treatment	Incubation conditions	
		Variables	Constant parameters
Surface soil	Temperature effect	T=10, 20, 30	θ_g=0.3
	Water content effect	θ_g=0.3, 0.7, 2.0	T=20
	Wet–dry cycles	θ_g=0.3–2.0	T=20
Subsurface soil	Temperature effect	T=10, 20, 30	θ_g=10.0
	Wet–dry cycles	θ_g=4.0–10.0	T=20

θ_g is soil water content in g-water g-soil^{-1} and T is temperature in degree of Celsius.

conditions are shown in Table 1. There were three treatments for surface soil and two treatments for subsurface soil. Only surface soil was examined for water content effects because subsurface soil was generally saturated under normal agricultural practices and the changes in θ_g were less dramatic than that of surface soil. In the temperature treatment experiment, both surface and subsurface soils were incubated at 10, 20 and 30 °C with θ_g of 0.3 and 10 g-water g-soil^{-1}, respectively. These two water contents were selected because they represented typical θ_g before the growing season, at which time the surface soil was dry and subsurface soil was submerged below the water table. To examine water content effects, surface soil was incubated at 0.3, 0.7 and 2.0 g-water g-soil^{-1} at 20 °C, corresponding to pre-irrigation (air-dry), post-irrigation (>50% saturation) and flooded conditions (saturation), respectively. The water potentials corresponding to 0.3 and 0.7 g-water g-soil^{-1} were estimated as <-10 kPa and about -1 kPa, respectively, using a bulk density of 0.130 g cm^{-3} and a water retention curve for peat soil (Naasz et al., 2005; Yoshikawa et al., 2002).

In the wet–dry cycle experiment, surface soil was incubated through three wet–dry cycles from flooding (θ_g=2.0 g-water g-soil^{-1}) to dry conditions (θ_g=0.3 g-water g-soil^{-1}) at 20 °C. Subsurface soil was also incubated through three flooded and non-flooded cycles (not dry), corresponding to a θ_g of 10.0 and 4.0 g-water g-soil^{-1}, respectively. Different values of θ_g were used for the two soils because of differences in water holding capacity. At the initial flooding conditions, at least 5 cm of water was above soil layers. The θ_g of 4.0 g-water g-soil^{-1} in subsurface soil represented nearly saturated conditions that occured when the water table was lowered for draining. The water potential of subsurface soil for θ_g at 4.0 g-water g-soil^{-1} was estimated at about −5 kPa, using a bulk density of 0.103 g cm^{-3} for untreated peat soil (Wells and Williams, 1996). This treatment mimicked fluctuations of the water table during irrigation practices.

A total of eighteen 1-liter Mason jars were setup for each incubation treatment of temperature, water content, and wet–dry cycle (Fig. 1). Each jar contained 35 g (dry weight) of surface soil or 15 g (dry weight) subsurface soil. The synthesized carbon-free solution with an EC_{25} of 0.5 dS m^{-1} and a SAR of 5 was sprinkled onto the soils to reach the desired θ_g. After water content adjustment, all jars were placed in corresponding constant temperature chambers in the dark. Each jar was covered by a lid with a 2-mm opening to allow for gas exchange. The θ_g in each jar was monitored every other day by gravimetric measurement. Deionized water was added when a 5% or more change in θ_g occurred. Deionized water was used to avoid salt accumulation and maintain constant salinity in each treatment. In the wet–dry cycle incubation, surface and subsurface soils were initially flooded with a θ_g of 2.0 and 10.0 g-water g-soil^{-1}, respectively. All jars were incubated at 20 °C and were uncovered so that soil samples were allowed to dry naturally through evaporation. When the soils reached the desired θ_g values, soils were reflooded to their initial θ_g with deionized water for further incubation.

For DOC determination, three replicates of each incubation condition were terminated at days 7, 21, 28, 42, and 60 (Fig. 1). A 15 g dry-weight equivalent soil was added to the synthesized solution to prepare a 1:10 (w:w) soil to solution mixture and shaken at 4 °C for 4 h. Samples were centrifuged for 20 min at 16,270 *g* relative centrifugal force at 4 °C. Supernatants were filtered through a 1.2 μm glass fiber filter (Fisher G4) and then through a 0.45 μm

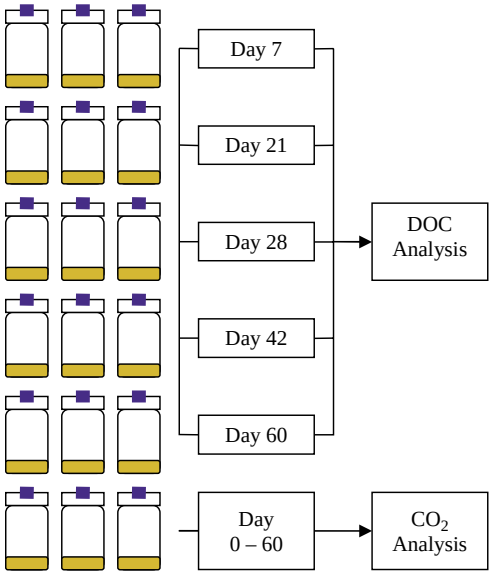


Fig. 1. Experimental design of incubation study. The numbers in the boxes indicates the day when the three jars were sacrificed for DOC extraction. The last three jars for CO_2 measurement were re-used over the course of the incubation.

membrane filter (Supor-450). All samples were refrigerated at 4 °C before analysis within a week. In addition to the DOC extraction, three replicates of each treatment were used to monitor CO_2 evolution during the 60-d incubation. The three jars for gas measurement were sealed with a gas-tight lid equipped with a removable rubber septum. The septum was used to seal the opening for 24 h before each sampling for CO_2 analysis. One ml of headspace was withdrawn from the sealed jar for determining CO_2 production. After sampling, the septum was removed. CO_2 was measured approximately twice a week. In addition, a total of nine empty jars (three at each temperature) were used to determine CO_2 background levels. CO_2 production from soils was determined by subtracting the CO_2 concentration of the empty jar from the corresponding soil-temperature treatment.

2.3. Analysis

Saturation extracts were used to characterize the soluble cations and anions of surface and subsurface soils (Rhoades, 1996). After standing overnight, soil solutions in the saturation pastes were collected by sequential vacuum filtration through a 1.2 μm glass fiber filter (Fisher G4) and a 0.45 μm membrane filter (Supro-450). A Shimadzu HPLC equipped with conductivity detector was used to analyze the concentrations of cations and anions. A 5 g soil sample (oven dried at 55 °C for 48 h) was combusted at 450 °C for 12 h to determine its ash and soil organic carbon contents. The loss on ignition (LOI) was assumed to be from the oxidation of soil organic matter. Soil organic carbon (SOC) content was estimated by a correlation for marsh soils: $SOC = 0.40[LOI] + 0.0025[LOI]^2$ (Craft et al., 1991). θ_g was determined at 55 °C to avoid excessive organic carbon oxidation for peat soils (Gardner, 1986). Carbon dioxide was analyzed by a HORIBA PIR-2000 infrared CO_2 analyzer. All water extracts were analyzed for DOC, UVA, EC_{25}, and pH. DOC was determined by UV-promoted persulfate oxidation using a DOHRMANN DC-180 carbon analyzer. UVA was determined by a diode array spectrophotometer (Hewlett Packard 8452A). A YSI model 32 conductance meter and Beckman Φ71 pH meter were used to determine EC_{25} and pH, respectively.

The composition of DOC extracted from soils before and after the 60-d incubation was characterization by XAD-fractionation (Aiken et al., 1992). Twenty ml capacity columns were used; these columns can process a 1 liter sample with a DOC concentration of no greater than 20 mg l^{-1} for maximum adsorption efficiency. Samples were acidified to pH 2 with 12.1 M HCl and passed through the XAD-8 column. The XAD-8 effluent was passed through an XAD-4 column. Samples were passed through both columns at a rate of 4 ml min^{-1}. Each column was then back eluted with 100 ml of 0.1 M NaOH at a rate of 2 ml min^{-1}. The eluates were collected in volumetric flasks and acidified to pH 2 with 12.1 M HCl. The eluate from XAD-8 is defined as hydrophobic acid (HPOA) and the eluate from XAD-4 is defined as transphilic acid (TPHA). The hydrophobic neutral (HPON) and transphilic neutral (TPHN) fractions are those compounds that adsorb onto the XAD-8 and XAD-4 resins, respectively, but are not dissolved during the back elution with NaOH. The hydrophilic acid (HPIA) fraction is the carbon in the XAD-4 effluent (Leenheer and Croue, 2003).

2.4. Calculation and statistical analysis

The C mineralization rate was determined on a daily basis and expressed in μg-C g-$soil^{-1}$ d^{-1}. Because CO_2 evolution was not determined every day, C mineralization rates between sampling intervals were assumed equal to the average of the two C mineralization rates from the two sampling events. Total C mineralization during the 60-d incubation was equal to the summation of C mineralization rates from day 0 to day 60. C mineralization rates on the days when DOC was determined were used to examine the relationship between CO_2–C and DOC. The least squares method was used to construct the best fit line between C mineralization rate and DOC concentration. The slope of each linear regression line was equal to the reaction rate constant for the specific incubation condition. The temperature coefficient (Q_{10}) was calculated as the reaction rate constant at temperature (T + 10) °C divided by the reaction rate constant at temperature T °C. The t-statistic was employed to test for differences among treatments and examine whether the intercepts and the slopes of the regression lines were significantly different from zero. Carbon-normalized UVA, known as specific UVA (SUVA), was calculated by dividing UVA by DOC concentration. The unit of SUVA in this study was expressed as l mg-C^{-1} m^{-1}. A paired t-test was employed to test for differences in DOC, SUVA, and HPOA and HPIA contents before and after the 60-d incubation.

3. Results

3.1. General soil properties

General characteristics of the surface and subsurface soils are shown in Table 2. In particular, DOC concentration in the surface soil was about 10 times higher than that of the subsurface soil, although the subsurface soil had a higher SOC content. The surface soil had appreciably higher salt contents (∼7×) than the subsurface soil. Salt was accumulated during the summer irrigation season due to evapotranspiration from the soil surface layers.

3.2. Surface peat soil

3.2.1. Temperature effect

Fig. 2 shows the variations of C mineralization rates and DOC concentrations in surface soil incubated at 10, 20, and

Table 2
Saturated soil extract analyses of the surface and subsurface peat soils (mean ± standard deviation, $n=4$)

Parameters	Surface soil (0–0.5 m)	Subsurface soil (2.5–3 m)
Saturated soil extract analyses		
pH	6.6 ± 0.1	6.7 ± 0.2
Electrical conductivity (dS m^{-1})	4.4 ± 0.1	0.6 ± 0.1
Dissolved organic carbon (mg l^{-1})	296 ± 7	21 ± 3
Inorganic carbon (mg l^{-1})	19 ± 7	2.3 ± 0.3
Na^+ (mg l^{-1})	505 ± 20	63.4 ± 7.3
K^+ (mg l^{-1})	12.8 ± 0.2	6.4 ± 0.4
NH_4^+ (mg l^{-1})	9.0 ± 0.8	6.4 ± 1.0
Ca^{2+} (mg l^{-1})	233 ± 7	14.7 ± 1.6
Mg^{2+} (mg l^{-1})	175 ± 3	12.1 ± 1.8
Cl^- (mg l^{-1})	1092 ± 12	167 ± 11
SO_4^{2-} (mg l^{-1})	897 ± 23	21.9 ± 4.5
Other soil properties		
Ash content (%)	49.9 ± 0.8	39.4 ± 3.0
Soil organic carbon (%)	26.4 ± 0.5	33.5 ± 2.1

30 °C with θ_g of 0.3. Under these conditions, both C mineralization rates and DOC concentrations had maximum values at the beginning of the incubation, decreased rapidly in the first week, and became relatively stable during the remainder of the incubation. On the first day, average rates of C mineralization were 18.3, 40.3, and 49.2 μg-C g-soil^{-1} d^{-1} at 10, 20 and 30 °C, respectively; within a week, the average rates dropped to 1.5, 5.7, and 9.8 μg-C g-soil^{-1} d^{-1}, respectively. Total CO_2–C losses during the 60 d incubation were 187, 406 and 612 μg-C g-soil^{-1} at 10, 20 and 30 °C, respectively.

DOC concentrations showed no trend with temperature, although temporal patterns for DOC concentrations were similar to C mineralization rates (Fig. 2a and b). The maximum value of DOC was 400 μg-C g-soil^{-1} at the start of the incubation and rapidly decreased to between 240 and 270 μg-C g-soil^{-1} at day 7. From day 7 to 60, DOC concentrations were relatively stable and average concentrations ranged from 220 to 250 μg-C g-soil^{-1}. Changes in DOC (ΔDOC) during the first week were −130, −150, and −160 μg-C g-soil^{-1} at 10, 20, and 30 °C, respectively. At day 60 of the incubation, ΔDOC was not significantly different ($p>0.05$) from day 7. Importantly, total C losses to mineralization (187–612 μg-C g-soil^{-1}) in the 60-d incubation exceeded ΔDOC (150–180 μg-C g-soil^{-1}) and there was no simple relationship between DOC concentration and incubation temperature.

3.2.2. Water content and wet–dry cycle effect

C mineralization of surface soils increased with θ_g in the range of 0.3 to 2.0 (Fig. 3). Under non-flooding conditions with θ_g of 0.3 and 0.7, maximum C mineralization rates occurred on the first day and were 40.3 and 120.5 μg-C g-soil^{-1} d^{-1}, respectively. In the flooded condition ($\theta_g=2.0$), the highest respiration rate occurred at day 3 (63.5 μg-C g-soil^{-1} d^{-1}). From day 8 to 60, C mineralization rates

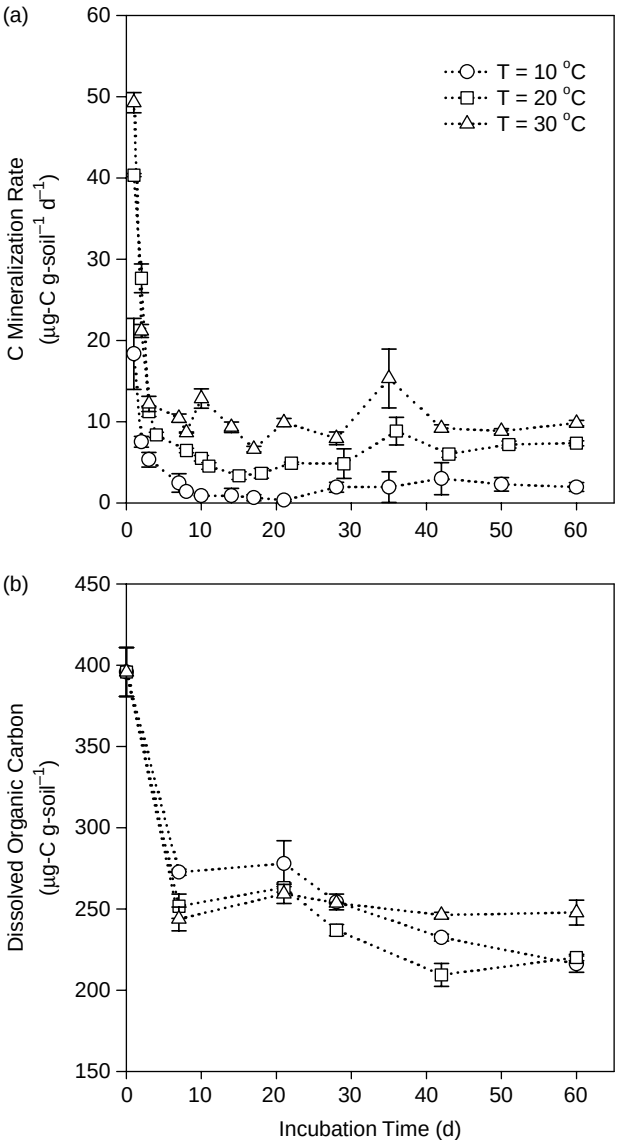


Fig. 2. Temperature effects on CO_2 and DOC productions in surface peat soil with θ_g at 0.3. Error bar represents the standard deviation of the measured values.

gradually decreased from 24.5 to 13.5 μg-C g-soil^{-1} at θ_g of 0.7 and from 35.3 to 20.2 μg-C g-soil^{-1} d^{-1} at θ_g of 2.0. At the end of the 60 d incubation, total CO_2–C losses were 406, 1200, and 1697 μg-C g-soil^{-1} at θ_g of 0.3, 0.7, and 2.0, respectively.

In the wet–dry cycle experiment, C mineralization rates varied with soil water content (Fig. 3b). The highest C mineralization rate occurred a few days after re-flooding and the lowest C mineralization rate occurred at the end of each wet–dry cycle when the soil had the lowest θ_g. Furthermore, C mineralization rates decreased with increasing numbers of wet–dry cycles: maximum values of 58.5, 38.7 and 22.5 μg-C g-soil^{-1} d^{-1} for the 1st, 2nd and 3rd re-wetting, respectively. Total C losses as CO_2 evolution in the 60-day incubation in wet–dry cycle treatment was 1445 μg-C g-soil^{-1}, which was significantly higher

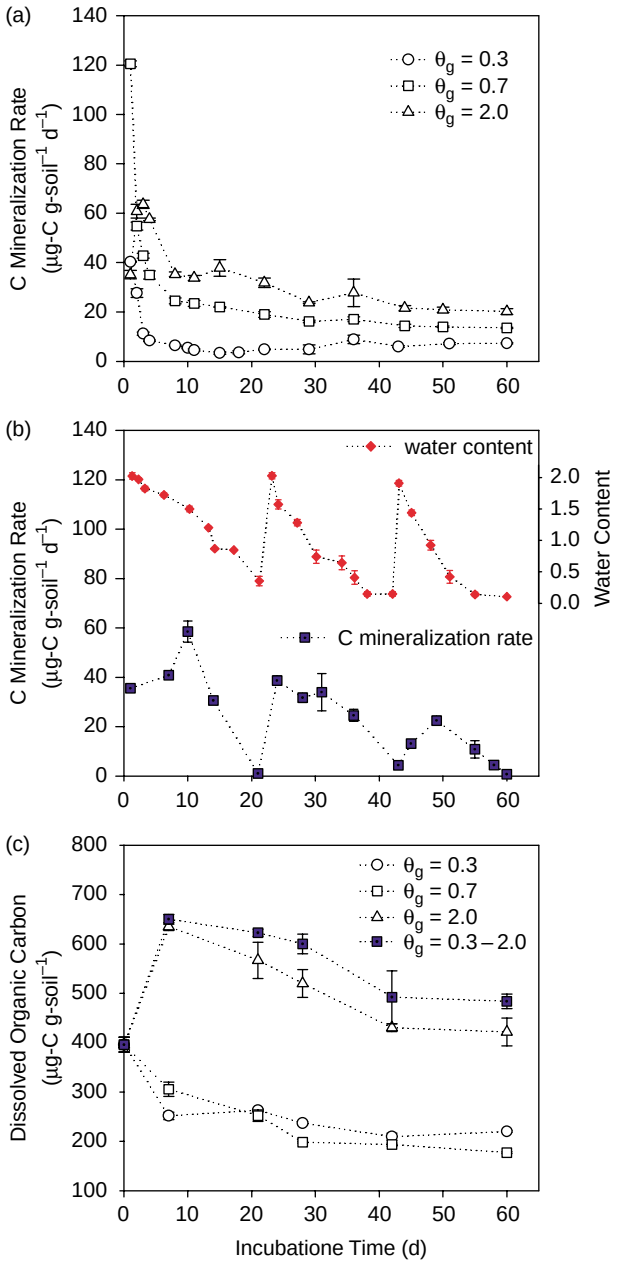


Fig. 3. Water content and wet–dry cycle effects on CO_2 and DOC productions in surface peat soil at 20 °C. Error bar represents the standard deviation of the measured values. Figure a represents the C mineralization rates at 3 different levels of θ_g. Figure b represents the C mineralization rates changed with water content in wet–dry cycle treatment. Figure c shows the DOC concentrations in the 60-d incubations.

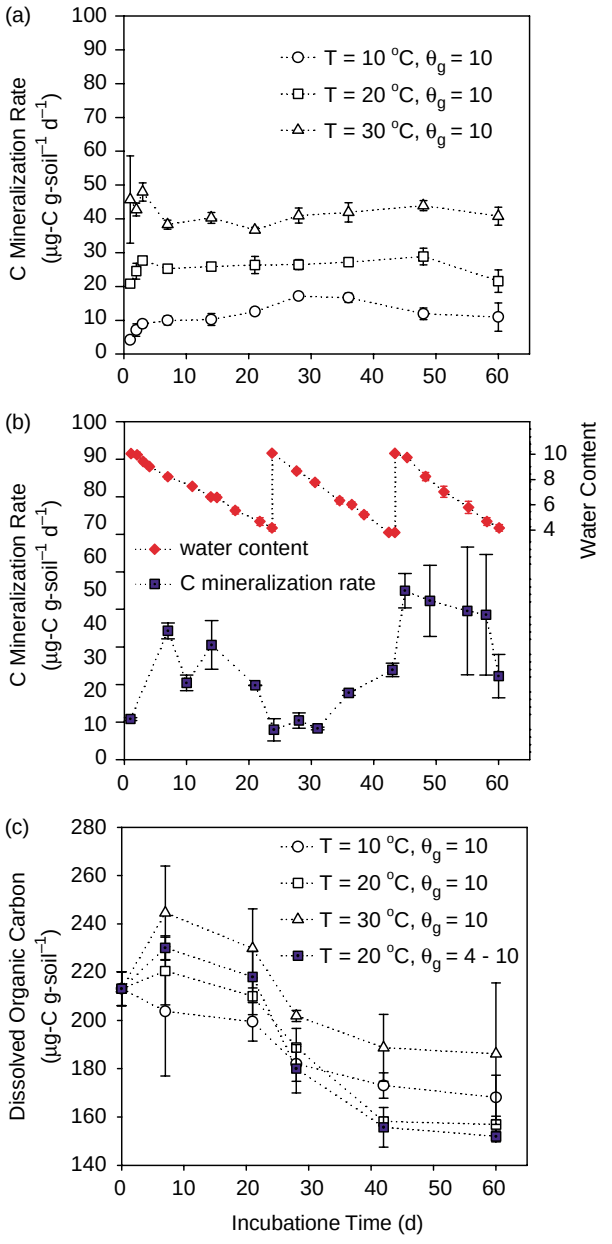


Fig. 4. Temperature and water content effects on CO_2 and DOC productions in subsurface peat soil. Error bar represents the standard deviation of the measured values. Figure a represents the C mineralization rates at 3 different temperature with θ_g at 10. Figure b represents the C mineralization rates changed with water content in wet–dry cycle treatment. Figure c shows the DOC concentrations in the 60-d incubations.

($p<0.01$) than that from soil at θ_g of 0.7 but lower ($p<0.01$) than that from soil at θ_g of 2.0.

Fig. 3c shows DOC concentrations in surface soil incubated at 20 °C with different θ_g. Soils experiencing flooding events ($\theta_g=2.0$), including wet–dry cycles ($\theta_g=0.3$–2.0), showed increased DOC concentrations compared to soils incubated only under non-flooded conditions ($\theta_g=0.3$ and 0.7). Under flooded conditions, the initial DOC concentrations increased by more than 50% compared to initial conditions (from 400 to about 640 µg-C g-soil^{-1} for $\theta_g=0.3$–2.0 and $\theta_g=2$). DOC gradually decreased with increasing incubation time and dropped to 420 and 500 µg-C g-soil^{-1} at day 60 for θ_g of 2 and θ_g of 0.3 to 2, respectively. DOC concentration at the end of each wet–dry cycle was lower than the previous cycle. In contrast, DOC concentrations in soils incubated at non-flooded water contents ($\theta_g=0.3$ and 0.7) decreased in the first week and became relatively stable over the remainder of the incubation.

3.3. Subsurface peat soil

C mineralization rates as a function of temperature in subsurface soils were relatively stable throughout the entire incubation period (Fig. 4a and b). C mineralization rates for the 60-d incubation averaged 11.2, 25.7, and 42.1 μg-C g-soil^{-1} d^{-1} at 10, 20, and 30 °C, respectively. At the end of the 60-d incubation, total CO_2–C losses were 695, 1449, and 2264 μg-C g-soil^{-1} at 10, 20, and 30 °C, respectively. In the wet–dry cycle incubation, C mineralization rates for surface and subsurface soils behaved distinctly different. The last wet–dry cycle had the highest C mineralization rate but with large variation (Fig. 4b). Also, there was no change in C mineralization rates after the 2nd rewetting. The total CO_2–C loss during the 60-d wet–dry treatment incubation was 2177 μg-C g-soil^{-1} and was significantly higher ($p<0.01$) than the subsurface soils incubated under continuously flooded conditions at 20 °C (1449 μg-C g-soil^{-1}). DOC concentrations in subsurface soils showed a general decrease after the first week to values ranging between 150 and 190 μg-C g-soil^{-1} (Fig. 4c). No significant correlation was found between DOC concentration and temperature. The DOC concentration of wet–dry cycle treatments matched closely with that of the continuously flooded treatment ($\theta_g=10$), although the C mineralization rates of these treatments behaved differently (Fig. 4).

3.4. DOC characterization

DOC collected from both soils after the 60-d incubation was characterized for SUVA and XAD fractionation (Table 3 and Fig. 5). For the surface soil, HPOA was the largest component, comprising about 50% of DOC. HPIA was the next most dominant fraction comprising 20 to 30% of DOC. Compared with DOC from the original samples, the 60-d incubation did not alter the overall DOC characteristics (Fig. 5a); HPOA and HPIA remained the most dominant fractions. However, certain incubation conditions may have a tendency to alter various XAD fractions. For example, wetter incubation increased the proportion of HPOA. Surface soil incubated at θ_g of 0.7 and 2.0 significantly increased the proportion of HPOA ($p<0.05$). The wet–dry cycle incubation appeared to increase the HPOA content, although the increase was not statistically significant ($p>0.05$). Surface soil incubated at higher temperatures (20 and 30 °C) contained a higher proportion of HPIA than the original sample ($p<0.05$).

For the subsurface peat soil, HPOA and HPIA comprised about 40% and 30% of DOC, respectively (Fig. 5b). In contrast to the larger differences in HPOA and HPIA contents in surface soil DOC, subsurface soil DOC contained a similar proportion of HPOA and HPIA. The 60-d incubation did not change the DOC composition.

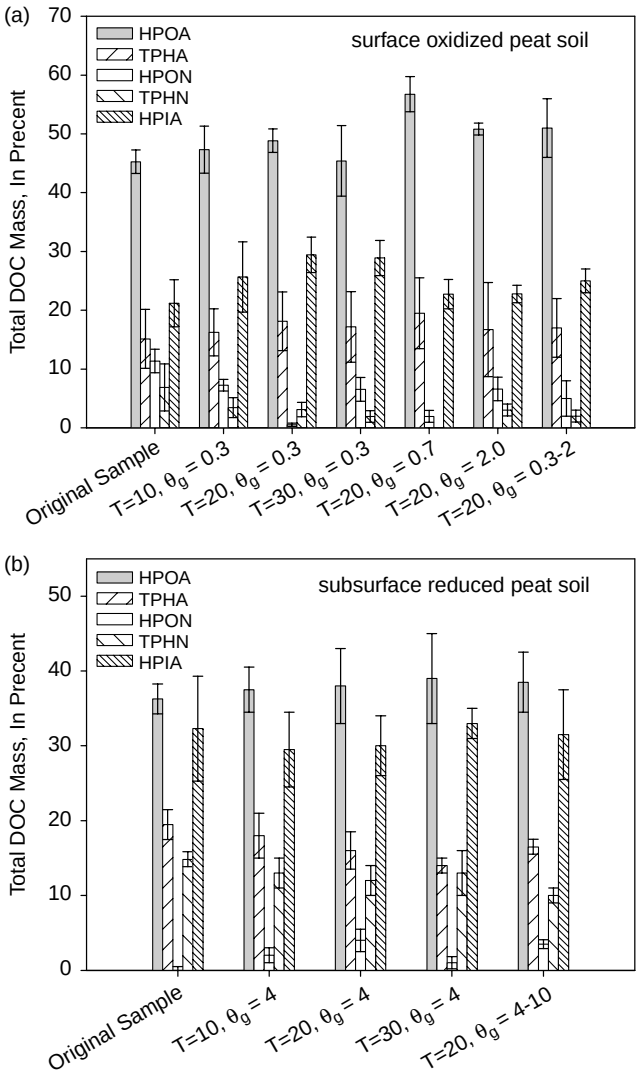


Fig. 5. Chemical fractionation of DOC from surface and subsurface soils after 60-d incubation under various temperature and water contents. Error bar represents the standard deviation of the measured values.

Table 3
SUVA of DOC from surface and subsurface soils after 60-d incubation under various conditions

Temp (°C)	θg (g g^{-1})	SUVA (l mg-C^{-1} m^{-1})
Surface peat soil		
Original sample		3.89±0.13
10	0.3	4.41±0.13
20	0.3	4.21±0.15
30	0.3	4.20±0.10
20	0.7	4.92±0.05*
20	2.0	4.52±0.11*
20	0.3–2.0	5.23±0.08*
Subsurface peat soil		
Original sample		1.80±0.09
10	10.0	3.11±0.20
20	10.0	2.54±0.10
30	10.0	2.70±0.50
20	4–10	3.22±0.20*

The asterisks indicated significant differences ($p<0.01$) compared to the original sample by paired t-tests. (mean±standard deviation, $n=3$).

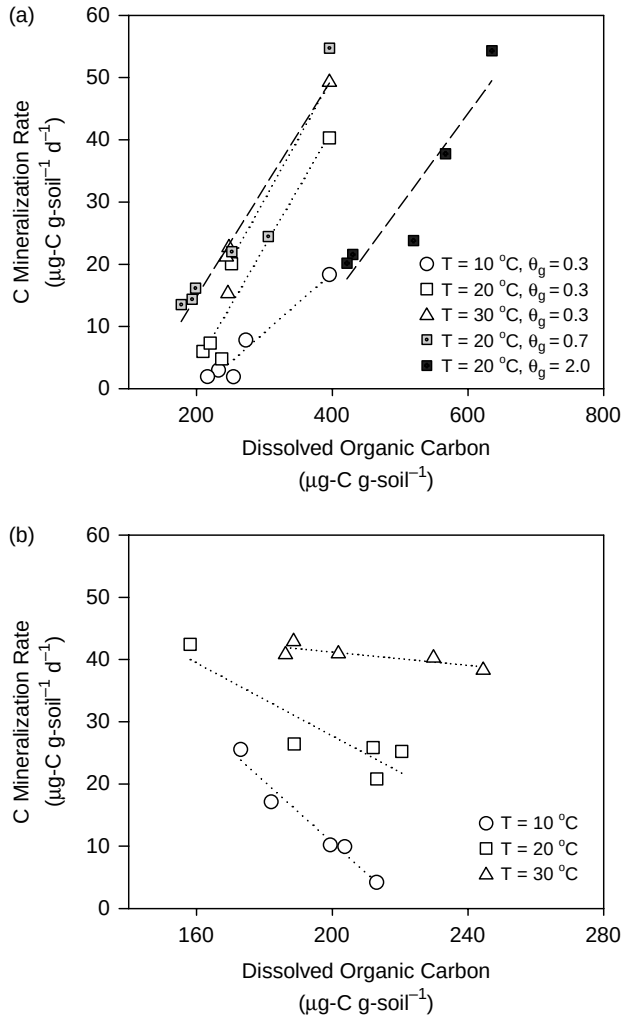


Fig. 6. C mineralization as a function of DOC concentration in both surface and subsurface peat soils. The dotted lines and dashed lines in Figure a represents temperature and moisture effects, respectively.

There were no significant changes in any fraction in the temperature and wet–dry cycle incubation treatments.

SUVA of DOC in both surface and subsurface peat soils increased after 60-d of incubation for all treatments (Table 3). Particularly, SUVA was significantly higher ($p<0.05$) than the original samples in wetter treatments of surface soil and wet–dry cycle treatments of both surface and subsurface soils. Although increasing temperatures increased SUVA of DOC after 60-d in both soils, the increases were not statistically significant ($p>0.05$).

3.5. Relationship between DOC concentration and C mineralization

Fig. 6 shows correlations between DOC concentrations and C mineralization rate of surface and subsurface soils under various incubation treatments. Linear regressions were constructed for constant temperature or water content treatments (Table 4). The linear equation represents first-order kinetics because the rate of CO_2–C production is proportional to the DOC concentration (i.e. $d[CO_2\text{–}C]/dt = k(T)[DOC]$, where $k(T)$ is the rate constant at a given temperature T). The slope of the regression line is equal to the rate constant at that condition. For example, the rate constants of CO_2–C evolution were 0.096, 0.189, and 0.197 d^{-1} for the surface soil at 10, 20, and 30 °C with θ_g of 0.3, respectively (Table 4). There were no significant ($p>0.05$) correlations between CO_2–C and DOC in the wet–dry cycles treatments.

Statistical analysis for the slopes of all the regression lines shows a correlation between DOC and CO_2–C with $p<0.05$, except for the subsurface soil incubated at 30 °C, which has a p-value of 0.07. Also, non-zero y-intercepts were observed in all linear regressions. However, not all y-intercepts were statistically different from zero with $p<0.05$. Surface soil incubated at 30 °C with θ_g of 0.3, 20 °C with θ_g of 0.7, and 20 °C with θ_g of 2.0 had a p-value greater than 0.05, but smaller than 0.1.

Q_{10} values were calculated for the temperature ranges of both soils. For surface soil, Q_{10} was equal to 1.98 and 1.04 for the increase of temperature from 10 to 20 °C and 20 to 30 °C, respectively. For the subsurface soil, Q_{10} was equal to 0.60 and 0.18 for the increase of temperature from 10 to 20 °C and 20 to 30 °C, respectively. We believe the rate

Table 4
Linear regressions of C mineralization rate ($d[CO_2]/dt$) and concentration of dissolved organic carbon ([DOC]) from surface and subsurface peat soils under various incubation conditions

Temp (°C)	θg (g g^{-1})	Linear correlation $y=mx+b$	r^2
Surface oxidized peat soil			
10	0.3	$d[CO_2]/dt = 0.096 \times [DOC] - 19.6$	0.95
20	0.3	$d[CO_2]/dt = 0.189 \times [DOC] - 34.1$	0.91
30	0.3	$d[CO_2]/dt = 0.197 \times [DOC] - 28.7$	0.96
20	0.7	$d[CO_2]/dt = 0.175 \times [DOC] - 20.3$	0.90
20	2.0	$d[CO_2]/dt = 0.149 \times [DOC] - 45.2$	0.87
Subsurface reduced peat soil			
10	10.0	$d[CO_2]/dt = -0.491 \times [DOC] + 108.7$	0.96
20	10.0	$d[CO_2]/dt = -0.293 \times [DOC] + 86.2$	0.81
30	10.0	$d[CO_2]/dt = -0.054 \times [DOC] + 50.9$	0.70

The units of $d[CO_2]/dt$ and [DOC] are µg-C g-soil^{-1} d^{-1} and µg-C g-soil^{-1}, respectively. m and b in the linear regression are the slope and the y-intercept, respectively.

constant from the linear relationships is an apparent rate constant that combines the rate constant of several reactions. A conceptual model explaining this phenomenon is described in the discussion section.

4. Discussion

4.1. DOC production

The incubation experiments indicated that the highest concentrations of DOC were released from the surface peat soil, under flooded conditions. Although subsurface peat soil contained a higher portion of soil organic matter, its DOC concentration was 2 to 3 times less than the surface soil. High concentration of DOC was collected from the surface soil was probably due to the crop debris and plant residues incorporated in the surface soil, which could yield highly water soluble organic carbon, such as proteins, cellulose, and polysaccharide (Aoyama, 1996; Boyer and Groffman, 1996; Stevenson and Cole, 1999). Significant increases of DOC from surface soil only occurred in soils that were flooded (i.e. continuously flooding or wet–dry cycles). An increase in soil temperature and/or soil water content at non-flooded conditions increased microbial activity as indicated by increased CO_2 evolution from soil respiration, but neither factor increased DOC concentrations.

Results indicated that DOC was produced primary during the initial flooding of the soils. Neither continuous flooding nor reflooding in wet–dry cycles enhanced DOC production. Thibodeaux and Aguilar (2005) described this DOC production process in surface peat soil as a two-step DOC release model, including (i) tea-bag type release processes for the quick release fraction and (ii) a slow-release fraction produced by continuous microbial processing. The rapid increase in DOC at initial flooding was an abiotic process resulting from the quick-release fraction of DOC from the soil substrate bed (Aguilar and Thibodeaux, 2005). Continuous flooding could further release DOC from the soil substrate bed at a constant rate over time through on-going microbial and fermentation processes (Thibodeaux and Aguilar, 2005). The fact that DOC concentrations decreased over the incubation period while the C mineralization rate was relatively unchanged implies that consumption by microbial respiration exceeded the rate of DOC production (Fig. 3).

4.2. Wet–dry cycles

Patterns for DOC concentrations in both soils experiencing wet–dry cycle incubation closely matched that of the continuous-flooding incubation (Fig. 3c and 4c). In contrast, C mineralization rates fluctuated with changes in θ_g and behaved differently from flooded treatments (Figs. 3a vs b and 4a vs b). Different C mineralization rates between wet–dry cycle and continuous-flooding treatments were expected because soil water is a key factor regulating C mineralization rates. Under similar environmental conditions, C mineralization rates are generally considered an indicator of C availability to microorganisms. Different C mineralization rates in samples with comparable DOC concentrations suggest that DOC is not the only C substrate for mineralization. This result agrees with the study by Lundquist et al. (1999) who found that DOC content is not a reliable indicator of C availability to microorganisms. Continuous flooding or drying processes did not increase DOC concentrations in these peat soils. In contrast, DOC concentrations from day 10 to day 60 in both wet–dry cycle and continuous flooding treatments were slightly decreased, which supported a previous finding that showed a large portion of DOC is not biodegradable (Zsolnay and Steindl, 1991).

The effects of wet–dry cycles on C mineralization of surface and subsurface soils were different. C mineralization rates decreased with increasing numbers of wet–dry events in the surface soil, whereas the C mineralization rate in the subsurface soil had the highest rate during the last wet–dry cycle. The results from the surface soils were consistent with those from other studies; the greater the number of rewetting events a soil experiences, the less CO_2 released after each rewetting (Fierer and Schimel, 2002). Wet–dry events can alter microbial community structure and microbial biomass may be altered (Fierer and Schimel, 2002; Lundquist et al., 1999). In contrast to the surface soil, the subsurface soil had experienced long-term anaerobic conditions (permanently reduced environments) and contain fibrous peat materials. Repeated wet–dry cycles enhanced the penetration of oxygen and promoted the degradation of raw peat materials. This may explain the increased C mineralization rates with increasing number of wet–dry cycles.

4.3. Compositional changes in DOC

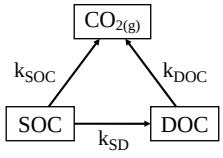
The SUVA and HPOA content in the surface soil were significantly increased ($p<0.05$) only for the wet–dry cycle and wetter ($\theta_g=0.7$–2.0) incubation treatments. These results agree with findings of a previous study using forest soils, in which HPOA concentration was linearly correlated with soil water content (Christ and David, 1996). SUVA has been used as a surrogate for aromatic carbon in soil and aquatic humic substances (Novak et al., 1992; Traina et al., 1990). Higher SUVA values indicate that there was an increase in the relative proportion of aromatic carbon in the DOC fraction. The increases in these two parameters are coherent because aromatic carbon is a main component in HPOA (Aiken et al., 1992). Compared to microbially labile organic carbon fractions, such as carbohydrates and proteins, the aromatic carbon fraction is relatively stable (Kalbitz et al., 2003). Thus, consumption of microbially labile organic carbon by microorganisms during

the incubation could increase the relative proportion of aromatic carbon. The increased aromatic carbon or HPOA content in soil waters implies that drainage waters from flooded peat soils can degrade the quality of Delta waters exported for drinking water. Aromatic carbon is a major reactive moiety for disinfection byproduct formation (Norwood et al., 1987, 1980) and the HPOA fraction has been shows to contain a higher proportion of aromatic carbon and other disinfection byproduct precursors than other DOC fractions (Croue et al., 2000; Owen et al., 1993). Not only do flooding and wet–dry cycle events enhance DOC production in surface soils, but they also increase the relative proportion of disinfection byproduct precursors. Thus, reducing flooding and wet–dry cycles could appreciably attenuate DOC leaching from Delta peat soils. Also, the 60-d incubation in both temperature and wet–dry cycle treatments did not stimulate DOC production nor change the DOC composition in subsurface soil. Maintaining a shallow groundwater table at the agricultural field could minimize DOC or disinfection byproduct precursor production from the subsurface soil zone.

4.4. DOC–CO_2 relationships

Linear correlations between C mineralization rates and DOC concentrations were observed in both the surface and subsurface peat soils (Table 4 and Fig. 6). C mineralization rates increased with an increase of temperature or soil water content, whereas DOC exhibited no relationship with these two parameters. Furthermore, both positive and negative correlations were observed between C mineralization rates and DOC concentration. Only positive correlations between C mineralization rates and DOC concentrations in soil have been previously reported (Cook and Allan, 1992b; Lundquist et al., 1999). The nearly 50% decrease in Q_{10} values from 10–20 °C to 20–30 °C seems unreasonably large, although previous studies showed that Q_{10} in some soils decreased with increasing temperature (Howard and Howard, 1993). Q_{10} values less than 1.0 in subsurface soils appeared contrary to first-order kinetics that imply that DOC is the substrate for CO_2 production. These apparently contrary results were attributed to multiple sources of organic carbon for C mineralization in these peat soils. Importantly, the total C losses from C mineralization over 60 d exceeded initial DOC concentrations for all incubation treatments. Both SOC and DOC can be substrates for CO_2 production (Boyer and Groffman, 1996). We believe that SOC, in addition to DOC, was mineralized by microbes and the rate constant in the equation is composed of two independent reactions. We propose a conceptual model using a kinetic approach to describe the DOC–CO_2 relationship in these peat soils (Fig. 7).

In this conceptual model, we assume that CO_2 production is a first-order reaction, and microbes using SOC and DOC as substrates possess reaction rate constants k_{SOC} and k_{DOC}, respectively. Total available organic carbon (TAOC) is the sum of SOC and DOC. TAOC is different from total organic carbon because not all organic C is available and accessible to microbes. Microbes can also produce DOC by utilizing SOC, but the reaction converting SOC to DOC is independent of CO_2 production and has an independent reaction rate constant k_{SD}. We assume k_{SD} is not equal to k_{SOC} because the mechanism producing CO_2 is probably different from that producing DOC (Christ and David, 1996;



[a] $\frac{d[CO_2]}{dt} = k_{SOC}[SOC] + k_{DOC}[DOC]$

[b] $\frac{d[CO_2]}{dt} = k_{SOC}([TAOC] - [DOC]) + k_{DOC}[DOC]$

[c] $\frac{d[CO_2]}{dt} = (k_{DOC} - k_{SOC})[DOC] + k_{SOC}[TAOC]$

[d] $\frac{d[CO_2]}{dt} = k_{app}[DOC] + k_{SOC}[TAOC]$

SOC	: Soil organic carbon	(μg-C g-soil^{-1})
DOC	: Dissolved organic carbon	(μg-C g-soil^{-1})
TAOC	: Total available organic carbon TAOC = SOC + DOC	(μg-C g-soil^{-1})
k_{SOC}	: reaction rate constant for C mineralization utilizing SOC to produce $CO_{2(g)}$	(d^{-1})
k_{DOC}	: reaction rate constant for C mineralization utilizing DOC to produce $CO_{2(g)}$	(d^{-1})
k_{SD}	: reaction rate constant for C mineralization utilizing SOC to produce DOC	(d^{-1})
k_{app}	: apparent rate constant for overall C mineralization	(d^{-1})

Fig. 7. A conceptual model describing CO_2 production in soils.

Moore and Dalva, 2001; Stevenson and Cole, 1999). The C mineralization rate ($d[CO_2]/dt$) is equal to the sum of CO_2 production from SOC and DOC, written as $k_{SOC}[SOC]$ and $k_{DOC}[DOC]$ in equation [a], respectively. By substituting SOC with TAOC and DOC, as shown in equation [b], and manipulating the equation algebraically, we obtained equation [c]: a linear relationship ($y=mx+b$) representing C mineralization rate in terms of DOC concentration, where y is the C mineralization rate ($d[CO_2]/dt$), m is the difference between reaction rate constants (k_{DOC}-k_{SOC}) alternatively called an apparent reaction rate constant (k_{app}), x is the DOC concentration, and b is the y-intercept and it is equal to TAOC concentration with a factor of k_{SOC}. This linear equation [c] can be used to explain the results of our incubation experiments.

Based on this model, the correlation between C mineralization rates and DOC concentrations depends on k_{app}, which is a function of k_{DOC} and k_{SOC}. If DOC contains more microbially labile C than SOC and the rate constant for mineralizing DOC (k_{DOC}) by microbes is greater than that for mineralizing SOC (k_{SOC}), k_{app} is positive. In most cases (Cook and Allan, 1992b; Lundquist et al., 1999) and in our incubation of surface peat soils, microbes consumed DOC faster than the consumption of SOC (i.e. $k_{DOC} >> k_{SOC}$). Also, k_{SOC} should be a very small number and he term $k_{SOC}[TAOC]$ can be neglected in the equation. Thus, the C mineralization rate was proportional to DOC concentration. The non-zero but negative y-intercepts in the linear correlations imply that a certain amount of DOC was not subject to mineralization within a limited time. This DOC is either recalcitrant or not assessable by microbes but is extractable by our extraction methods (Cook and Allan, 1992a; Gregorich et al., 2003; Kalbitz et al., 2003). In contrast, if SOC contains more labile C than DOC, k_{SOC} will be larger than k_{DOC}. The term k_{app} becomes negative and the C mineralization rate is inversely proportional to DOC concentration. This unusual case occurred in the subsurface peat soil. The C mineralization rate of the SOC in the subsurface peat soil was higher because the SOC contained mostly raw peat materials preserved for thousands of years due to anaerobic conditions resulting from submersion under water. Exposure of these labile peat materials to the aerobic environment in our incubation study caused rapid oxidization and mineralization (Moore and Knowles, 1989). Therefore, k_{SOC} was larger than k_{DOC} and the term k_{app} in the equation [c] becomes negative. Thus, the C mineralization rate exhibited a negative correlation with the concentration of DOC. The y-intercept of these linear correlations should be equal to k_{SOC} [TAOC].

This model also provides a plausible explanation for the abnormal behavior of Q_{10} in surface and subsurface soils. The calculated Q_{10} from the linear correlation between C mineralization rates and DOC concentrations represents the overall change in the apparent rate constant (k_{app}), two simultaneous reactions representing the consumption of DOC and SOC. These two independent reactions should have their own distinct rate constants and these rate constants may behave differently as temperature changes. We assume that the Q_{10} for the reactions mineralizing DOC and SOC, κ and ϕ, respectively, are constant over the temperature range of 10 to 30 °C. For surface soil, our results showed that the apparent Q_{10} values were 1.98 and 1.04 for 10 to 20 °C and 20–30 °C, respectively. With these boundary conditions, we solved for κ and ϕ and found that they were inversely related and fell within the range of 3.0–4.0. These values are consistent with the range reported from a previous study, which concluded that most Q_{10} values for C mineralization range from 2 to 4 (Howard and Howard, 1993).

In summary, this paper utilized a series of controlled laboratory experiments to examine factors affecting DOC production and C mineralization rates over a range of conditions experienced resulting from agricultural practices in peat soils from the Sacramento-San Joaquin Delta. We conclude that surface peat soil is a more important source of DOC compared to subsurface peat soils that have experienced long-term anaerobic conditions. DOC is mainly produced in surface peat soils following flooding or wet–dry cycles. DOC concentration was not correlated with incubation temperature or soil water content. However, there were linear correlations between C mineralization rates and DOC concentrations and these correlations were temperature and water content dependent. DOC–CO_2 mineralization relationships were best explained by a model consisting of C mineralization from two C substrates (SOC and DOC).

Acknowledgements

Thanks to Dr. Roger Fujii (U.S. Geological Survey) and Michael Mata (Department of Land, Air and Water Resources - UC Davis) for their assistance in field and laboratory work. This study was supported by the Water Resources Center, University of California (Project Number W-891). Alex Chow was also supported in part by an NIGMS MORE Institutional Research and Academic Career Development Award to UC Davis and San Francisco State University, http://prof.ucdavis.edu, grant number K12GM00679.

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